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Shock compression of polyvinyl chloride

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This study presents shock compression simulation of atactic polyvinyl chloride (PVC) using ab-initio and classical molecular dynamics. The manuscript also identifies the limits of applicability of classical molecular dynamics based shock compression simulation for PVC. The mechanism of bond dissociation under shock loading and its progression is demonstrated in this manuscript using the density functional theory based molecular dynamics simulations. The rate of dissociation of different bonds at different shock velocities is also presented in this manuscript. Published by AIP Publishing.

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I. INTRODUCTION

Polyvinyl chloride (PVC) is used as one of the major component materials for infrastructure, different types of transportation vehicles, and recreational sport commodities. There have been extensive studies on this material primarily to improve its mechanical properties1–3 and also to remove some of its undesirable properties such as dechlorination when subjected to UV lights4–8 through the use of different additives. Typically, these additives which are designed to stabilise the polymer and make it more resistant to degradation are usually not covalently bonded to the polymer and therefore can leach out over time, especially in harsh environments such as a marine environment.9 Thereby given the usage of these materials in defence and/or space applications (in which it is subjected to harsh environments), it is essential to determine the response of this material without any additives under extreme loading situations while in service (such as improvised explosive device (IED) explosion induced shock loads for defense vehicles, shock load due to hypersonic velocities of space vehicles).

In existing literature, there appears to be a very few studies on shock loading of PVC. This manuscript addresses this lacuna in research through combined molecular dynamics (MD) and ab-initio investigation of the material subjected to different shock intensities. Prior to this study, experimental researches10–12 on shock loading of PVC produced some of the principal Hugoniot plots, but detailed mechanism of the breakdown of the polymer chain under shock loading has not been investigated thoroughly. Moreover, because of the difficulty in measuring extreme pressures (in gigapascal range) and temperature (thousands of Kelvin) within a very short interval of time through experimental methodologies, molecular and atomic simulations are absolute complementary requirements to shock compression experiments. Deeper insights into the molecular/atomic level phenomena, which in turn defines the physical behavior and mechanism of polymers (PVC) subjected to high temperature and pressure within a very small time-period of the order of femto-seconds (characteristic of shock loads), can typically be obtained through molecular level investigations which this manuscript addresses.

Based on the usage of PVC, shock loading is inevitable, and thereby, a detailed study of this material under shock loading is important. Some examples as to where these materials are subjected to shock loads are as follows: (a) Low density PVC foams are used as core materials in sandwich composite panel construction of naval and aerospace vehicles to protect against explosion induced shocks, (b) recreational and/or sports devices and gears also use PVC materials which are many a times subjected to impact induced shock loads, (c) currently sandwich type construction are also being used in infrastructure industry where PVC is used as core material to protect against projectile loads during hurricane and tornadoes, as well as explosion induced shock loads due to IED or bombs placed nearby to the structure, where these materials are also subjected to shock loads, (d) used in parts of space vehicles which are subjected to hypersonic speeds (thereby shock loads) during its exit and reentry from the earth atmosphere. Carter and Marsh13 obtained the Hugoniot equation of state (EoS) of PVC through shock compression experiments. An experimental investigation on shock compression of thermoplastic atactic PVC has been carried out by Bourne and Millet11 in which the Us−Up relationship has been prescribed. An experimental study has also been carried out by Butler et al.14 in which the authors observed changes in slope to the Us−Up curve for PVC at around 20 GPa. The study (refer Refs. 10 and 11) speculated that the change in slope is due to some structural changes in the polymer. The detailed study (using classical molecular dynamics (MD) and density functional theory (DFT) based MD (DFT-MD)) in this manuscript apart from validating the Us−Up relationship obtained from experimental investigations also tries to address the speculations regarding structural changes in the polymer under shock loads.14 The manuscript also highlights changes in temperature with the increase in pressure, changes in bond lengths at different time instances of shock loading, mechanics, and sequence of different bond breakages (if any) at...
different shock intensities. It should be noted that these
information cannot be obtained easily from experimental
investigations.

One of the major limitations of molecular dynamic (MD)
is that the accuracy of the results are dependent on the descrip-
tion of force potentials used to describe the molecular structure
of the polymer. Thereby, different force potentials (COMPASS, PCFF, and PCFF+) are used in this manuscript
to describe the PVC monomer and are compared against results
obtained from experimental investigations. It is well known
that UV radiation causes dechlorination in PVC; thereby, it is
of interest to determine if similar dechlorination is observed
when PVC is subjected to shock loads. However, the classical
force fields are unable to demonstrate bond breakage; thereby,
density functional theory (DFT) simulations (using AM05 ex-
change correlation function) have been used in this manu-
script and compared against less computationally intensive
classical force fields. In this regard, it should be noted that
recentlyMattsson et al.14 studied the fidelity of many classical
and/or reactive forcefield (Reax FF, AIREBO, OPLS, Borodin
and Smith exp-615) and compared them against DFT-MD sim-
ulations (based on AM05 exchange correlation function16) at
high temperature and pressure for the case of polycarbonates
such as polyethylene (PE) and PMP and demonstrated that the
density functional theory based molecular dynamics (DFT-
MD) study at the cost of increased computation gives better
results in comparison to the classical and/or reactive force-
fields. However, it should be noted here that halogenation in
PE resulting in PVC makes it a different class of polymers
which has not been investigated in literature subjected to shock
loads using first and MD based simulations studies.

Pure PVC is considered for our simulations. Even
though the presence of molecular structural defects, like al-
lylic chloride, tertiary hydrogen, and chlorine atoms, and end
groups, such as double bonds, oxygen containing groups,
peroxide residues, are known to cause degradation in the
polymer,17 these defects have been considered outside the
scope of this work. In order to stabilize the dechlorination
in the presence of UV light, different types of cross-linking
agents along with their methods of addition have been pro-
posed by researchers,18–21 which is also kept outside of the
scope of work for this study.

This manuscript will thereby strive to investigate the
behavior of pure PVC under shock loads of different intens-
ities by answering the following questions:

• Are most popular classical force fields for polymers such
  as PCFF, COMPASS, and PCFF+ valid in the case of
dynamic shock wave simulation?
• How far in pressure and temperature scale these classical
  forcefields can describe polymer macromolecule
  conformation?
• Does DFT based MD calculation show convincing fidelity
  in describing the events of shock compression?
• How does different radial distribution functions (RDFs)
of different bonds evolve with change in shock speeds?
• How and when the disintegration of bonds start when sub-
  jected to a range of shock velocity? Does the backbone
  of the pendant group disintegrate first or is it the side-chains?
• What is the percentage of different bond dissociation
  under different shock loads?

II. SIMULATION METHODOLOGIES

To obtain a model of pure PVC bulk cell, a series of
steps are followed. First, a long chain consisting of 150 vinyl
chloride monomer (VCM) is created. As the stereo-
regularity (tacticity) (i.e., spatial isomerism) in vinyl poly-
mers has a great role over the polymer properties, special
care is taken during the assignment of pendant group around
the asymmetric segment of the vinyl-type repeat units,
$(-\text{CH}_2 - \text{CHR} - )$. The created model of the PVC chain has
a tacticity of 50%, and the polymerization is in a head-to-tail
fashion. After creating PVC chains, 15 chains are taken in a
bulk cell to generate the initial configuration of a condensed
amorphous model PVC. Monte-Carlo (MC) based lengthy
mixing simulation is carried out to create amorphous PVC
at ambient temperature and pressure. A total of 13 530 atoms
are simulated to get a periodic bulk cell of model condensed
phase amorphous PVC with dimension of $55.3948 \, \text{Å} 
\times 55.3948 \, \text{Å} \times 55.3948 \, \text{Å}$. The amorphous builder module
of Material Design, Inc.,22 has been utilized for this polymer
modelling purpose. The generated initial configuration is
directly readable by LAMMPS.23 After creating the model
PVC, different forcefields like PCFF, COMPASS, and
PCFF+ are assigned to atom types and atomic charges.
Since the average initial density of the PVC sample in the
experimental investigation13 is 1.376 g/cm$^3$, the initial den-
sity used in the simulation is kept close to the experimental
initial density (1.374, 1.369, and 1.371 g/cm$^3$ for PCFF,
COMPASS, and PCFF+, respectively).

As DFT calculations are very costly and computa-
tionally power consuming, a separate amorphous PVC model
structure has been developed as the initial configuration
for DFT based MD calculation. Other factors such as polymer-
ization coefficient, density, and polymerization fashion
(head-to-tail here) have been kept unaltered in these simul-
ations in comparison to the MD simulations with classical
force fields. A total of 248 atoms are simulated for creating a
periodic bulk amorphous cell with dimension of
$14.34 \, \text{Å} \times 14.21 \, \text{Å} \times 14.8747 \, \text{Å}$ with an average mass density
of 1.3681 g/cm$^3$ at ambient temperature and pressure. The
initial configurations are shown in Figure 1. We believe that
since the crucial interfering factors are same for both cases,
the obtained results are comparable; a difference in the num-
ber of atoms in simulations should not thereby affect the
essential generality of the physics behind these computa-
tional experiments. Similar to this study, reduced atoms for
performing DFT calculations have been taken and compared
against MD simulations.14

Three classical forcefields belonging to second genera-
tion class II type potential (differs from each other based on
chronological improvements in the non-bonded interactions)
have been used in the present work along with a first princi-
ple based study. The polymer consistent forcefield (PCFF)24
is based on CFF9125 and is extended so as to have a broad
coverage of organic polymers, (inorganic) metals, and zeo-
lites. Most parameters in the force field PCFF are derived
based on HF/6-31G* energies, energy derivatives, and electrostatics potentials that are subsequently scaled to correct the systematic calculation error. The nonbonded van der Waals parameters of PCFF, which include atomic partial charge and Lennard-Jones 9-6 parameters, are taken from liquid structure and energy simulation of simple silanes. Reliability and accuracy of PCFF forcefield has been tested by comparing molecular structure and conformational energies of polysilanes against gas phase experimental data. It has been observed that even though this forcefield perform well in many different situations, these do not provide accurate results for molecular dynamic simulations at finite temperature. In order to account for the effect of finite temperature “condensed phase optimized for atomistic simulation studies” (COMPASS), the forcefield has been developed, which has been chosen as one of the forcefields for simulations in this manuscript. PCFF+ has also been chosen as another forcefield for our set of simulations. PCFF+ is an all-atom type forcefield based on PCFF with extensions and refinements, in particular, for non-bonded parameters, which have been derived as part of Materials Designs R&D effort in a similar manner to that employed in the earlier development of the COMPASS forcefield.

Apart from the classical forcefields, the density functional theory based molecular dynamics (DFT-MD) study has also been carried out as part of this study. The density functional theory (DFT) is a widely used quantum mechanical simulation technique for calculating ground state energy, properties of bulk material, and molecular energy surface for periodic systems. Despite being such a widely used method, the accuracy of the calculations typically depends on the choice of the particular exchange correlation function. Multipurpose Armiento-Mattson (AM05) exchange correlation functional has been selected for this study since the functional contains no empirically determined parameters and also because the functional improves over the local density approximation (LDA) by reproducing two model systems with known solutions: the uniform electron gas and the surface jellium. Moreover, this AM05 functional reportedly shows significant fidelity for different materials such as semiconductors, simple metals, transition metals, alkali-halides, and oxides.

For all classical forcefield based simulations, we applied successive minimization and equilibration to get atactic PVC model at desired temperature of 300 K. The energy minimization algorithm has been utilized in an iterative manner with a tight tolerance limit to obtain an energy minimized initial structure of amorphous PVC. After such equilibration and minimization, the final structures of the amorphous atactic PVC are generated with almost equal density for different forcefields. The final periodic bulk PVC sample has been utilized to simulate shock wave propagation through these models by applying multiscale shock technique (MSST), developed by Reed et al. Instead of simulating a shock wave within a large computational cell with many atoms, the computational cell in MSST algorithm (implemented within the LAMMPS framework) follows a Lagrangian point through the shock wave which is accomplished by time evolving equations of motion for the atoms, as well as volume of the computational cell to constrain the stress in the propagation direction to the Rayleigh line and the energy of the system to the Hugoniot energy condition. Computational cell size for MSST simulation has been so chosen such that the stress, density, and energy density do not vary appreciably along the length of the computational domain (a requirement for MSST in which the stress and energy of a molecular dynamic simulation is constrained to obey the momentum and energy Hugoniot relations such that the simulation proceeds through the same thermodynamic states as would occur in a steady shock). The computational cell size should not also be too small such that boundary effects play a role in the simulation. MSST method for simulating shock propagation is reportedly an efficient and convenient technique, particularly for long timescale simulations. The shock Hugoniot points are calculated by using this method for all classical forcefield simulations up to 500 ps with a timestep size of 1–0.1 fs depending on the shock intensity. It should be noted here that periodic energy rescaling has been done as a part of this method to ensure better conservation of energy. No profound drift in energy, in terms of departure from Hugoniot line (in temperature unit) and Rayleigh line (in pressure unit), has been observed within the timescale of the simulation. The molecular trajectories are then eventually post-processed to investigate the further shock induced
phenomena, such as molecular conformations at high pressure and temperature, successive ordering and/or disordering of molecules/polymer chains, etc.

In DFT calculations, the principal Hugoniot points are obtained by applying an iterative compression procedure from an equilibrated initial reference state to a specific Hugoniot state point by increasing the kinetic energy. Once the material is compressed instantaneously, it is allowed to relax till it reaches a steady state. The cycles of loading are continued until the measured thermodynamical variables satisfy the Rankine-Hugoniot equation, \((U - U_0) = 1/2(P + P_0)(V_0 - V);\) where the subscript zero signifies the initial values. For calculating the ramped temperature Hugoniot points, isothermal isochoric (NVT) ensemble (using Nose-Hoover thermostat) is applied for 10–15 ps with a timestep size of 0.5–0.1 fs depending on the shock strength. The plane wave cutoff is chosen above 750 eV by monitoring the subsequent convergence of the stress-tensor.\(^{33}\) All the DFT-MD calculations are accomplished by using the VASP package.\(^{34,35}\) Although slightly different shock simulation methods are applied for DFT and classical MD calculations, no significant sensitivity over the simulation methods have been observed. The details of the DFT-MD simulations, carried out as part of this work, follow from similar types of studies and observation for other types of polymeric systems by Mattsson et al.\(^{14}\)

III. RESULTS AND DISCUSSION

The results obtained from the simulations are compared and validated with experimental observations (which typically provide information of the Hugoniot planes). Since the results obtained vary with an average initial density of the sample, the average mass density of the samples used for simulation in this manuscript are kept at 1.371 g/cm\(^3\) (a value close to that of experimental investigation—it should be noted that typically it is very difficult to obtain the exact desired target density after minimization and equilibration).

A. Hugoniot planes

In Figure 2, the calculated mean-stress and average mass density at shock equilibrium state for different forcefields and DFT results are plotted and compared against PVC shock experiment data of Carter and Marsh.\(^{13}\) The shock pressure, i.e., the shock induced mean stress is computed by using the hydrostatic part of the stress tensor consisting of kinetic energy tensor along with virial stress tensor (which includes all degrees of freedom—bond vibrations, angle bending, torsional, out of plane dihedral and improper along with the pairwise energy contribution which comes from van der Waal and coulombic interactions). It can be observed that up to ~12.5 GPa of pressure and density of ~2.02 g/cm\(^3\) (in the shock equilibrated state), all the classical forcefields, PCFF, COMPASS, and PCFF+, show reasonable agreement with experiment. PCFF is observed to underestimate mass density after ~4.75 GPa of shock pressure, thereby deviating from experiment by ~2.57% at a pressure of 8.5 GPa. With the increase in shock pressure up to 70 GPa, PCFF deviated from experimental observations of mass density by ~7.36%. On the other hand, forcefields PCFF+ and COMPASS show good correlation with experimental observation till a mean stress of ~20 GPa. In fact, later in the manuscript, it has been demonstrated that bond dissociation starts at ~20 GPa due to which the DFT based simulations produce better match with experimental investigations in comparison to the classical forcefields. Thereby the upper limit of using classical forcefields for shock compression of PVC can be taken as ~20 GPa. The tendency of underestimation of the mass density by classical forcefields hints at the possibility of failure to describe properly the macromolecule conformation of PVC when it is getting deformed via compaction, which is directly related to the non-bonded electrostatic interaction. Re-parameterization and training of functionals against sets of experiments can be done to make the above mentioned non-reactive classical forcefields more accurate and applicable (which is outside the scope of this manuscript), which eventually might enhance the capability for deciding bond creation and/or breakage at such high temperature and pressure situation based on bond increment charging algorithm, currently being used by researchers to accomplish the polymeric cross-linking phenomenon. Moreover, it can be seen readily from Figure 2 that re-parameterization and refinements in the non-bonded terms of the classical forcefields makes it substantially softer with respect to previous forcefield, which enables it to achieve closer proximity to experimental Hugoniot points. Beside the enhancement of accuracy, the chronological refinements of non-bonded parameters from PCFF to PCFF+ indicate the crucuality and sensitivity of the treatment of the non-bonded parameters over the property of the polymer at a finite temperature and pressure.

Figure 3 demonstrates a similar pattern as that observed in Figure 2, in which up to a shock velocity of 3.5 km/s (i.e., a shock pressure \(P = 4.75\) GPa and average density\(\rho = 1.84\) g/cm\(^3\)) PCFF shows convincing capability to describe shock induced PVC macromolecular conformations, whereas other two candidate forcefields COMPASS and
FIG. 3. Shock compressed shock velocity–particle velocity \( (U_s-u_p) \) Hugoniot plane of polyvinylchloride using classical forcefield based MD and DFT-MD simulation methods. Comparison are made between simulation results and experimental shock Hugoniot data by Carter and Marsh.\(^{31}\)

FIG. 4. Comparison of shock induced pressure-temperature (P-T) Hugoniot plane of PVC using classical MD and DFT-MD simulations.

PCFF+ show greater fidelity than PCFF up to 6.0 km/s (i.e., shock pressure \( P = \sim 20 \) GPa and average density \( \rho = \sim 2.22 \) g/cm\(^3\)). In this range of pressure (i.e., \( 0 \) – \( 20 \) GPa and density, \( 1.38 \sim 2.22 \) g/cm\(^3\)), an overestimation of particle velocity tendency (maximum deviation 9\%) is observed for PCFF, although beyond this region, it underestimates the particle velocity by 10\% for a specified shock velocity. As we mentioned earlier that after 20 GPa of pressure, i.e., shock velocity of 6.0 km/s (which in other words, after volume compression of \( \sim 60\% \)), classical forcefields expectedly do not resemble convincing correlation with experiment unlike DFT-MD simulation since long PVC macromolecular chains undergoes breaking.

Another important Hugoniot point is temperature which is very challenging to measure with sufficient accuracy experimentally, since available optical pyrometric methodologies are not that reliable due to large uncertainties.\(^{36}\) One typically has to assume an equation of state (EoS) based on which temperature can be obtained. As soon as a shock starts propagating through the medium, the temperature of the sample will rise instantaneously due to increase in kinetic energy of the molecules. Once the shock front travels a significant distance, depending on the relaxation time of a particular target material, it achieves a shock equilibrated state. In our simulation, we are calculating the shock equilibrated temperature of the PVC sample, which can indicate if there occurs any shock induced reaction, melting or co-existence of phases, etc. As there is no available experimental shock temperature data of PVC, we have refrained to validate our simulation data with experimental investigations; rather, we will discuss qualitatively over the possible physical events in shocked PVC and also the aspect of comparing classical potentials against DFT. Figure 4 shows pressure vs. temperature (P-T) plots obtained using different classical forcefields along with first principle studies. Since there is a significant difference of mean-stress and density obtained from previous figures, it can be well expected that there would be significant differences in the temperature calculation also. The temperature is evaluated directly from kinetic energy of the atoms by applying the well known equipartition theorem. It should be mentioned here that since there is a lack of treatment of effect of ground state electronic contribution over temperature for the classical forcefields, the temperature calculations from the classical models may be erroneous.\(^{37}\) Therefore, large deviations can be observed between the classical potential results with that of DFT-MD calculations. Since quantum nuclear vibrational effects (due to presence of covalent bonds) are considered for DFT simulations, temperatures calculated from DFT are usually more accurate compared to classical forcefields.\(^{37}\)

It has been reported in literature that the glass transition temperature \( T_g \) (temperature at which a polymer transitions from a hard, glassy material to a soft, rubbery material) for PVC is \( \sim 350 \) K. The temperature attained at 3.5 km/s shock speed is more than the value of \( T_g \) and thereby, the state of PVC may undergo a change with shock velocities at and above 4 km/s. It is quite possible that the monomer may undergo dissociation as it attains the glass transition temperature \( (T_g) \). Thereby variation of specific heat, \( c_v \), is plotted along with Hugoniot temperature to observe any distinctive changes in the slope above the Dulong-Petit limit, which might indicate changes in short range correlation and eventual molecular dissociation. Figure 5 represents plot of normalized \( c_v \) vs. temperature. The value of \( c_v \) has been evaluated as \( c_v = \frac{(\partial E/\partial v)_P}{\rho v P} \), where \( \Gamma = -(\nu/T)(\partial T/\partial P) \) is the Gruneisen parameter, and \( E, v, P, \) and \( T \) corresponds to energy, volume, pressure, and temperature, respectively. Subscript \( H \) and \( s \) stands for along the Hugoniot and along the isentrope (for more details, see Ref. 38). For further details on the evaluation of \( c_v \) from Hugoniot temperature, one is referred to Ref. 38. A distinctive change in slope of \( c_v \) can be observed above the temperature of 749.06 K, which indicates a possibility of molecular dissociation. Radial distribution function (RDF) is presented in Section III B, which confirms the occurrence of molecular dissociation.
Radial distribution functions

Radial distribution function (RDF) of all the species (within a PVC monomer) has been investigated for all shock velocities ranging from 3.0 km/s to 10.0 km/s, (i.e., pressure range 0 to 70 GPa and temperature from 300 K to 3500 K) to reveal the exact state of the shock compressed PVC. Here, it should be mentioned that since the accuracy and applicability of classical potentials for shock compaction simulation are observed up to 20 GPa of shock pressure (from Subsection III A), we have adopted only DFT based MD shock simulation results for further investigation regarding shocked state of the specimen. In this subsection, pair distribution function of carbon-chlorine (C-Cl), carbon-hydrogen(C-H), and carbon-carbon(C-C) atoms is discussed to investigate the shock induced phase transition and chemical dynamics of the corresponding molecular bonds. In DFT calculations, we are not using any particular molecular class like classical potentials; rather, we are dealing with each atom separately. Thereby, the so-called bond definition refers to the existence of two atoms at a specified separation distance apart over a certain instance of time (which is usually taken as 10 fs). Usually, the initial/equilibrium separation distance between two bonded atoms is obtained from the abscissa position of the first coordination shell peak in the radial distribution function plot of the specific atom set. If the separation distance between two atoms exceed a certain specified proportion of the initial separation distance over a certain interval of time (typically referred to as the cutoff radius), then the bond is taken to be dissociated. The cutoff radius for neighbor counting around any site is chosen as 37% larger than the equilibrium bond distance of the respective chemical bonds. Although this cutoff based neighbour counting technique to analyze appearance or disappearance of any chemical bonds in DFT based atomistic simulation is standard and convenient, still the actual chemical composition of any system depends on the cutoff radius. It should be noted here that it has been proved earlier that the estimation of the sample density at which significant dissociation initiates or takes place is not sensitive to the cutoff radius. Since the equilibrium bond distances are 1.53 Å for C-C, 1.11 Å for C-H, 1.85 Å for C-Cl(methylene), and 2.65 Å for C-Cl (methyl) bonds, the threshold cutoff radii for the simulation are chosen as 1.9 Å for C-C, 1.50 Å for C-H, 2.53 Å for C-Cl(methylene), and 3.63 Å for C-Cl (methyl) bonds.

Figure 6(a) shows C-Cl(methylene chloride) pair distribution function for the entire pressure-temperature (P-T) range considered in this manuscript. At ambient temperature and pressure, the first sharp and prominent peak corresponding to the first coordination shell for the C-Cl (methylene chloride) pair distribution function is observed at 1.85 Å (referred to as methine C-Cl equilibrium bond length) accompanied by a second coordination shell peak at 2.61 Å. With the increase in pressure and temperature (associated with increase in shock velocity), thermal broadening of the first coordination shell is observed. The intensity of the peaks also decreases, suggesting lower population density of C-Cl (methine) pair particles. It should be pointed out here that RDF is a measure of the probability of finding a particle at a distance from a given reference particle; thereby, a decrease in peak-intensity of the first coordination shell demonstrates lower population density of the corresponding pair of atoms. For shock velocities more than 6 km/s, a significant loss of coordination of the bond can be observed by complete disappearance of second coordination shell peak. As mentioned before, considering the prescribed cutoff distance as 2.48 Å for the methine C-Cl bond, it is observed that bond dissociation starts at a shock velocity of 6.0 km/s. The percentage of bond breakage increases along with the increase in the shock intensity.

At ambient temperature and pressure conditions, the C-Cl (methyl) bond length is observed as 2.65 Å (refer Figure 6(b)). Since the methyl C-Cl bond has a higher dipole moment (as a result of the presence of two hydrogen atoms bonded with a carbon, thereby making the carbon atom more electropositive) compared to methine C-Cl bond, it can be expected that the bond length of methyl C-Cl would be more than that of the methine C-Cl bond. Similar to that of methine C-Cl bond, thermal peak broadening can be observed along with the increase in the shock velocity. In fact, along with the increase in the shock speed, the kinetic energy of the system increases which typically reduces the peak-intensity of the first coordination shell, thereby demonstrating lower population density of the adjacent atom. This phenomenon is observed for both the C-Cl bonds. The main difference between the RDFs of the two C-Cl bond is the presence of second coordination shell peak for the methine C-Cl bond at ambient condition and lower shock velocities. Apart from this, the methyl C-Cl bond also shows less stability than the methine C-Cl bond, which has been discussed later in the section on polymer dissociation mechanism, even though bond dissociation is observed to be initiated at the same shock speed for both the C-Cl bonds.

The first coordination shell for both the C-H bonds is 1.11 Å (refer Figure 7). The primary difference between the two C-H bond is in the observance of the relative intensity of
the second and third coordination shell (in comparison to the intensity of the first coordination shell). The reason for this can be traced to the presence of strongly electronegative chlorine (Cl) atoms linked to the carbon (C) atom which influences the population density of the second and third coordination shell in comparison to that of the first coordination shell. Differences can be observed at higher shock speeds between the two C-H bonds. At or above 6 km/s shock speed, the C2-H RDF shows just one peak followed by a flat line whereas the C1-H RDF shows undulations where the peak intensity of the second coordination shell roughly matches with the population density of the first coordination shell. The presence of undulations hints at complete loss of coordination of the bond or periodicity of the bonds, thereby indicating amorphization/melting. Bond dissociation can be observed at a much later stage for the C-H bonds in comparison to the C-Cl bonds. Apart from these features, thermal broadening and the decrease in population density is also observed (just like any other bonds in the monomer) along with the increase in shock velocity.

The first coordination shell for the C1-C2 bond is 1.53 Å (Fig. 8). Thermal broadening and decrease in population density of the first coordination shell can be observed similar to the other RDFs along with the increase in the shock speed. Disappearance of the second coordination shell can also be observed at around 7 km/s shock speed. Dissociation of C1-C2 bond is observed to initiate at shock velocities above 7 km/s. In fact, C1-C2 bond is observed to be more stable than the C-Cl bond since the bond dissociation for these bonds occurs at higher shock velocities (higher pressure and temperature) compared to the C-Cl bonds.

Interestingly, it should be mentioned at this point that dechlorination is a known problem of PVC exposed to UV light, which is also being observed on shock loading of PVC in this study.

C. Molecular dissociation mechanism

Primarily it can be observed from trajectory analyses that bond breaking initiates at 6.0 km/s, i.e., after the density...
reaches 2.34 g/cm³. Typically on shock loading, the molecule gets compressed and the bond lengths start decreasing. This decrease in bond length occurs up to a certain limit after which the repulsion takes over and the bond eventually dissociates. At a shock velocity of 6 km/s, the methyl C-Cl bond first starts to dissociate within 75 fs of achieving the shock equilibrium state. After 3.5 ps of dissociation of methyl C-Cl bond, methine C-Cl bond is observed to dissociate. Thereby it can be stated that C-Cl(methine) bond shows greater lifetime than C-Cl(methyl) bond. Early bond dissociation of methyl C-Cl may be due to the higher dipole moment of the bond, which occurs due to the presence of the two hydrogen atoms bonded with a carbon, thereby making the carbon atom more electropositive in comparison to the carbon atom of the methine C-Cl bond. Interesting correlation can be observed between this DFT study and the observation made by Butler et al.¹¹ the onset of bond dissociation as obtained from this DFT-MD study is around 18.9 GPa whereas Butler et al.¹¹ observed a change in the slope in $U_s-U_p$ curve at a specified shock pressure of 22.3 GPa which they suggested might be due to some structural change in polymer chain. This manuscript in fact justifies the hypothesis of Butler et al.¹¹ that the change in $U_s-U_p$ slope as observed in experimental investigations is primarily due to bond dissociation, the conclusion for which is arrived from atomistic investigations carried out in this manuscript. The percentage of bond dissociation (shown in Figure 9(a)) is evaluated based on the number of bonds which have exceeded the bond lengths as prescribed by the threshold cutoff radius for that specific bond. At a shock pressure of 18.9 GPa and associated temperature at 898 K, a significant amount of C-Cl bond breaking is detected, which is around 22.4% and 20.1% (refer Figure 9(a)) for methyl and methine carbon-chlorine, respectively. Even though the percentage of bond dissociation is approximately the same initially for both the C-Cl bonds at a specific pressure and temperature, the methyl C-Cl bond disintegration rate is much higher at high shock velocities in comparison to the methine C-Cl bond. At a shock pressure of 18.9 GPa and C-H and C-C backbone bond dissociation is observed within the specified cutoff filter. Along with the increase in the shock pressure (26.6 GPa) at a shock velocity of 7.0 km/s, no significant amount (below 1%) of C-H bond breaking is observed, whereas at this shock state, 40% of the C-Cl bond is observed to be dissociated. At this shock intensity of 7 km/s (corresponding to a shock pressure of 26.5 GPa and density of 2.51 g/cm³), rapid rupture of the PVC backbone is also observed (20% amount of C-C backbone dissociated). At higher shock pressure corresponding to a pressure of 70 GPa, almost all the PVC chain gets dissociated and attains a warm, dense plasma like state. Even though bond dissociation of C-C bond starts later (at higher shock velocities compared to C-Cl bonds), the dissociation rate is significantly higher and in fact matches that of C-Cl methyl bonds at higher shock velocities. Interestingly, C-H bonds show significant lifetime under such extreme condition (around 70 GPa), and only up to 10% of C-H bonds are observed to have broken. Also, it can be observed that the rate of

FIG. 8. Comparison of carbon-carbon (C1-C2) radial distribution functions (RDFs) of PVC at ambient condition and shock compressed state for all shock velocities ($U_s$) of 3.0 km/s to 10.0 km/s with the increment of 1.0 km/s.

FIG. 9. (a) Comparison between % of dissociation of each bond at increasing shock intensity as obtained from DFT-MD calculation. (b) Snapshot of temporal evolution of molecular trajectories at shock velocity of 7.0 km/s. I-VI represents snapshot of MD trajectories from 25 ps to 35 ps, where oval shaped marker along with arrow typically indicates the sequential onset of bond dissociation. Yellow and red background is used to enhance the visibility of the surroundings of cite of dissociation. In the molecular trajectory, green, cyan, and black represents chlorine, hydrogen, and carbon atoms, respectively.
dissociation is significantly low for C-H bonds in comparison to other bonds.

Figure 9(b) shows the bond dissociation sequence at a shock velocity of 7 km/s. This shock velocity is chosen since at this shock velocity, both the C-Cl along with the C-C bond dissociates. It can be observed from the figure that after 25 ps of the passage of the shock front, methyl C-Cl bond dissociation is noticed. Figure 9(b)-(I)-(III) corresponds to the MD simulation time of 25, 26, and 27 ps where red color wide arrow indicates dissociation of methyl C-Cl bond and the yellow background is used to enhance the visibility of the sites of bond dissociation. At 28 ps (refer Figure 9(b)-(IV)), first methine C-Cl bond dissociation is observed, which has been indicated by wide blue arrow with the same yellow background. At a later stage of 30 and 35 ps (refer Figures 9(b)-(V) and 9(b)-(VI)), C-C and C-H bond dissociation is observed, which has also been indicated by green and deep blue arrows with red background. Similar type of sequences is observed for other shock velocities.

Similar type of DFT-MD studies showing bond dissociation has been presented in Ref. 14 for polyethylene (PE). It should be noted that typically chlorination of PE results in the formation of PVC. The study by Mattsson et al.,14 shows that for PE (initial density taken as 0.955 g/cm$^3$) the onset of dissociation (primarily associated with the C-C backbone bonds) starts at a density of 1.8 g/cm$^3$ with corresponding shock temperature of 1500 K and pressure of 44 GPa. Our study with PVC (initial density taken as 1.386 g/cm$^3$) shows onset of dissociation at a density of 2.41 g/cm$^3$ (T = 1067.41 K and P = 23.29 GPa). Thereby, the comparison of the two studies shows that onset of bond dissociation starts at a compression of 84.5% for PE compared to 97.2% for PVC. This may indicate that chlorination results in an enhancement of mechanical ductility. It can also be observed that the pressure range at which onset of dissociation starts in PVC (18.9 GPa for C-Cl bond and 23.2 GPa for C-C bond) is significantly smaller than that of PE (44 GPa for C-C bond), thereby indicating that global stiffness of C-C bond might have been reduced due to the presence of the highly electronegative chlorine atom in PVC compared to that of PE. However, it should be pointed out that a more detailed study needs to be carried out, which performs rigorous calculation of chemical properties (e.g., distribution of total local potential, evolution of charge density with shock pressure and temperature, energetics of molecular orbital, etc.) to conclusively comment on the chemical effect of chlorination on shock load, which is out of the scope of the present manuscript.

IV. CONCLUSION

Experimental observations indicated changes in $U_s-U_p$ slope at around 20 GPa pressure, it is speculated that PVC monomer undergoes bond dissociation at that shock load generated pressure ranges. This manuscript proves through molecular and/or atomic simulations that indeed bond dissociation occurs around that shock wave generated pressure and temperature ranges. It should also be pointed out that the bond dissociation mechanism in PVC starts after the material has reached the glass transition temperature. A detailed study involving both MD and DFT-MD simulations identified that classical forcefield based MD simulations (PCFF, COMPASS, and PCFF++) may only be appropriate prior to dissociation. Ab-initio simulations carried out as part of this work demonstrated the exact mechanism of bond dissociation in which C-Cl bond are observed to dissociate first (process referred to as dechlorination and quite commonly observed in PVC subjected to UV lights) compared to backbone C-C bonds. It is also observed that at higher shock velocities, the amount of dissociation of methyl C-Cl and C-C bonds is almost the same. The C-H bond is observed to be most stable even at high shock intensities.

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